Vibrational energy transfer in ultracold molecule - molecule collisions

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We present a rigorous study of vibrational relaxation in p-H_2 + p-H_2 collisions at cold and ultracold temperatures and identify an efficient mechanism of ro-vibrational energy transfer. If the colliding molecules are in different rotational and vibrational levels, the internal energy may be transferred between the molecules through an extremely state-selective process involving simultaneous conservation of internal energy and total rotational angular momentum. The same transition in collisions of distinguishable molecules corresponds to the rotational energy transfer from one vibrational state of the colliding molecules to another.

The creation of ultracold molecules has opened up new avenues for research in physics and chemistry. Ultracold molecules are finding exciting applications in condensed-matter physics [1], quantum information science [2], physics of elementary particles [3] and chemical reaction dynamics [4]. The experimental work on the production of dense ensembles of ultracold molecules is currently being pursued by many research groups [3]. The progress of the experiments relies on detailed understanding of molecular collisions at ultracold temperatures [5, 6]. Recent theoretical studies [7, 8, 9, 10] have provided important insights into atom - molecule inelastic and reactive collisions at cold and ultracold temperatures. The collision energy of ultracold molecules is usually much smaller than the energy spacing between ro-vibrational molecular levels and the duration of an ultracold collision is very long, which leads to unusual propensity rules and mechanisms of inelastic scattering. For example, vibrational relaxation in ultracold collisions of molecules with atoms was found to give rise to quasi-resonant energy transfer [11] resulting in extremely narrow distributions over final ro-vibrational states. Ultracold molecules in excited vibrational states are routinely produced in experiments on photoassociation and Feshbach resonance linking of ultracold atoms [12]. The lifetime of the molecules is limited by collision-induced vibrational relaxation. Dense ensembles of ultracold molecules can also be created in experiments on buffer gas cooling [13] or Stark deceleration of molecular beams [14]. Ground-state molecules may then be excited by black-body radiation [15] and release energy through vibrationally inelastic collisions. Laser cooling of molecules, when realized, will result in significant populations of vibrationally excited states that may relax through collisions in a gas of sufficient density [16]. Evaporative cooling of molecular ensembles to ultracold temperatures is based on energy dissipation in molecule - molecule collisions. The spectrum of accessible energy levels is much denser for collisions of molecules with each other than for collisions of molecules with atoms and it is important to understand dominant energy transfer mechanisms in molecule - molecule interactions at ultracold temperatures.

In this Letter, we present rigorous quantum calculations of cross sections for cold and ultracold collisions of p-H_2 molecules in different levels of vibrational and rotational excitation and identify a new mechanism for ro-vibrational energy transfer, not present in collisions of molecules with atoms. We find that the energy exchange process in collisions of indistinguishable molecules at cold and ultracold temperatures may be highly efficient and state selective when the internal energy and total rotational angular momentum of the colliding molecules are simultaneously conserved. By treating the H_2 molecules as distinguishable particles it is shown that this mechanism is primarily driven by a rotational transfer process. We show that the efficiency of the near-resonant energy transfer is largely insensitive to the initial vibrational excitation of the molecules.

The H_2 + H_2 system is the simplest neutral tetra-atomic system and it serves as a prototype for describing collisions between diatomic molecules. Using a model rigid rotor potential energy surface (PES) for the H_2-H_2 system developed by Zarur and Rabitz [17], Forrey [18] investigated rotational transitions in p-H_2 + p-H_2 collisions at ultracold temperatures. Boothroyd, Martin, Keogh and Peterson (BMKP) [19] have recently calculated a full-dimensional PES for the H_4 system. Pogrebnya and Clary [20] reported rate coefficients for collisions of p-H_2 and o-H_2 in the first excited vibrational state for collision energies between 10^{-3} eV (11.604 K) and 1 eV (11604 K). They included all internal degrees of freedom and used the BMKP PES in a quantum calculation based on the centrifugal decoupling approximation. Maté et al. [21] reported an experimental study of rotationally inelastic collisions at temperatures between 2 K and 110 K and compared their data to theoretical results obtained using the PESs calculated by Diep and Johnson (DJ) [22] and Schaefer and Köhler (SK) [23]. These potentials describe the interaction between H_2 molecules fixed at the equilibrium internuclear distance. Lee et al. [24] have recently presented a comparative analysis of cross sections for rotationally inelastic collisions between p-H_2 at low and ultralow energies computed using the DJ and BMKP PESs. Time-dependent approaches have also

been recently used to describe the dynamics between two p-H_2 [25, 26] and between p-H_2 and o-H_2 [27] at thermal energies.

The results presented here are obtained using the BMKP PES and a full-dimensional quantum dynamics calculation without any decoupling approximations. We employed a newly developed quantum scattering code [28] based on the formalism described by Arthurs and Dalgarno [29], Takayanagi [30], Green [31], and Alexander and DePristo [32]. We consider H_2 molecules initially in different quantum states characterized by the vibrational quantum number v and the rotational angular momentum j. We refer to a combination of two ro-vibrational states of H_2 as combined molecular state (CMS). A CMS represents a unique quantum state of the diatom - diatom system before or after a collision. The CMS will be denoted as $(vjv'j')$. We used a "well-ordered states" notation [30] where $v > v'$ or when $v = v'$, $j \geq j'$. As the colliding molecules are indistinguishable, the quantum numbers vj or $v'j'$ cannot be assigned to a particular molecule. To describe collisions of distinguishable molecules, we will use the notation $[vj; v'j']$, where the quantum numbers vj characterize one molecule, and $v'j'$ the other. The cross sections for state-resolved ro-vibrational transitions are obtained from the solution of coupled differential equations [31] using the log-derivative method of Johnson [33] and Manolopoulos [34], and appropriate scattering boundary conditions [29].

Fig. 1 presents the cross sections for elastic and inelastic scattering of H_2 molecules for collision energies from 10^{-6} K to 120 K. We consider collisions of H_2 molecules in the excited ro-vibrational states $(v = 1, j = 0)$ and $(v = 1, j = 2)$ with H_2 molecules in $(v = 0, j = 0)$ and collisions of $H_2(v = 1, j = 0)$ with $H_2(v = 0, j = 2)$. The cross sections for elastic collisions of H_2 molecules in the ground state $(v = 0, j = 0)$ are also shown. The calculations are performed for the total angular momenta $J = [0 - 10]$ and for both parities. While the elastic scattering cross sections for collisions of molecules in the vibrationally excited states are practically the same, the probability of inelastic scattering is extremely sensitive to the initial states of the colliding molecules. The inelastic relaxation of $H_2(v = 1, j = 0)$ is six orders of magnitude more efficient in collisions with $H_2(v = 0, j = 2)$ than in collisions with $H_2(v = 0, j = 0)$. The zero-temperature limiting values of the relaxation rate constants for (1000), (1200) and (1002), are respectively, 9×10^{-18}, 4×10^{-14} and 6×10^{-12} cm^3 s^{-1}. The inelastic cross section for collisions between $H_2(v = 1, j = 2)$ and $H_2(v = 0, j = 0)$ is smaller than the inelastic cross section for collision between $H_2(v = 1, j = 0)$ and $H_2(v = 0, j = 2)$ at low and ultralow energies. It undergoes a rapid enhancement of two orders of magnitude at the collision energy 25.45 K, at which both inelastic cross sections become similar.

To explain the results of Fig. 1, we have calculated the corresponding state-to-state cross sections for a collision energy of 10^{-6} K (see Fig. 2). The final CMSs are presented in the order of increasing energy. Figure 2 shows
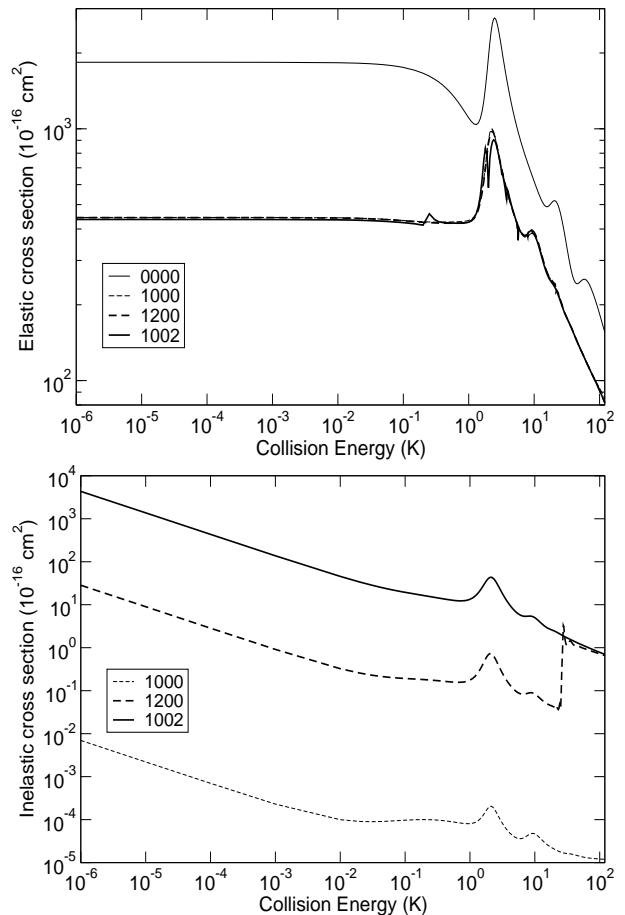

FIG. 1: Elastic (upper panel) and inelastic (lower panel) cross sections for H_2-H_2 collisions for collision energies from 10^{-6} K to 120 K. The curves are labeled by $(vjv'j')$ values. See text for details.

that ro-vibrational relaxation in molecule - molecule collisions is determined by the propensity to conserve the internal energy and the total rotational angular momentum of the colliding molecules. The cross sections for vibrational relaxation in collisions of $H_2(v = 1, j = 0)$ with $H_2(v = 0, j = 0)$ are rather small because the minimization of the energy gap between the initial and final CMS would require a large change of the total rotational angular momentum of the colliding molecules. Conversely, the conservation of the total rotational angular momentum would introduce a large energy gap. Consequently, there is no single dominant CMS in the final state-to-state distribution shown in panel a of Fig. 2. The inelastic relaxation of $H_2(v = 1, j = 2)$ in collisions with $H_2(v = 0, j = 0)$ shown in panel b of Fig. 2 is dominated by the transition $(1200) \rightarrow (1000)$. In this case, the energy gap and the difference in total rotational angular momentum of the two CMSs are simultaneously minimized. The inelastic relaxation of $H_2(v = 1, j = 0)$ in collisions with $H_2(v = 0, j = 2)$ is however highly efficient. It is dominated by the single transition $(1002) \rightarrow (1200)$,
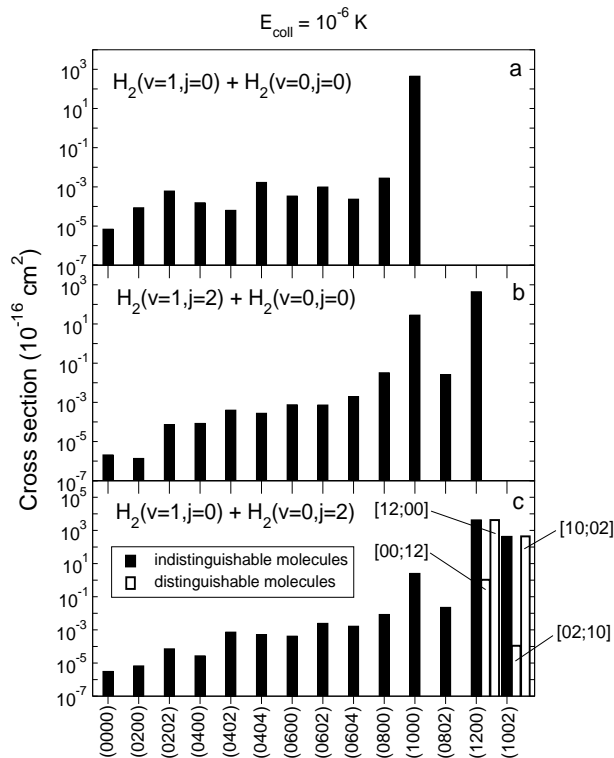
FIG. 2: State-to-state cross sections as functions of the final combined molecular state for the same systems as in Fig. 1 and for a collision energy of 10^{-6} K.

as shown in panel c of Fig. 2. This process conserves the total rotational angular momentum and has a very small energy gap of 25.45 K. The energy gap arises from the slightly different centrifugal distortion of the vibrational states $v = 0$ and $v = 1$. Therefore, the conservation of internal energy and total rotational angular momentum is largely satisfied and the process becomes highly efficient and selective. This near-resonant transition is 150 times more efficient than the transition $(1200) \rightarrow (1000)$. The reverse transition $(1200) \rightarrow (1002)$ is responsible for the rapid enhancement of the inelastic cross section for $H_2(v = 1, j = 2) + H_2(v = 0, j = 0)$ collisions at 25.45 K shown in Fig. 1 (the state (1002) becomes energetically accessible at this collision energy). The mechanism is thus a highly specific process, reminiscent of quasi-resonant energy transfer in collisions of rotationally excited diatomic molecules with atoms [11, 35, 36], but with a purely quantum origin.

In order to elucidate the mechanism for the $(1002) \rightarrow (1200)$ transition, we have repeated the calculation in Fig. 2 for the collision process $H_2(v = 1, j = 0) + H_2(v = 0, j = 2)$ assuming that the colliding molecules are distinguishable. The inelastic transition $(1002) \rightarrow (1200)$ in collisions of indistinguishable molecules corresponds to two transitions: $[10;02] \rightarrow [12;00]$ and $[10;02] \rightarrow [00;12]$ in collisions of distinguishable molecules. The first one corresponds to purely rotational energy transfer,

and the second to purely vibrational energy transfer. As follows from Fig. 2, the rotational energy transfer dominates over the vibrational energy transfer by three orders of magnitude. The inelastic transition $(1002) \rightarrow (1200)$ can thus be viewed mainly as the rotational energy transfer. These symmetry considerations can also explain why Panda et al. [27] found a surprisingly small cross section for the resonant distinguishable process p-$H_2(v = 0, j = 0)$ + o-$H_2(v = 1, j = 1) \rightarrow$ p-$H_2(v = 1, j = 0)$ + o-$H_2(v = 0, j = 1)$, despite a small energy gap of 8.5 K. The rotational energy transfer between $j = 0$ and $j = 1$ is forbidden due to symmetry so this transition is driven by the vibrational energy transfer. We conclude that the near-resonant transitions should be generally smaller in ortho-para collisions than in para-para collisions.
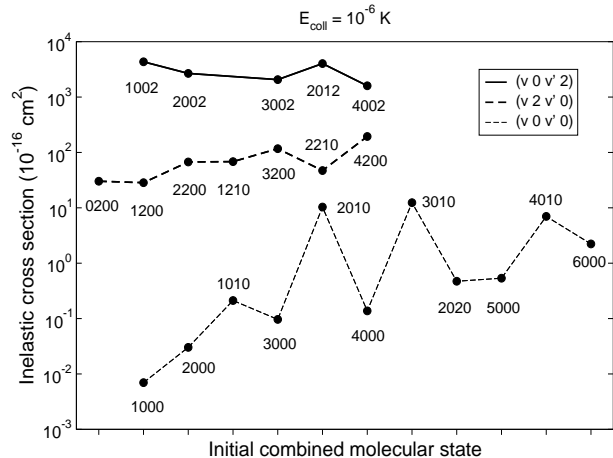

FIG. 3: Inelastic cross sections as functions of the initial combined molecular state for a collision energy of 10^{-6} K.

Fig. 3 demonstrates the effects of vibrational excitation of the colliding molecules on the inelastic relaxation cross section at a collision energy of 10^{-6} K. The results are presented as functions of the initial CMSs $(v0v'0)$ (dashed line), $(v2v'0)$ (dashed bold line) and $(v0v'2)$ (solid line). We use the full basis set for the calculation involving the initial CMSs $(0j0j')$, $(1j0j')$, $(2j0j')$ and $(1j1j')$ and truncated the basis set, as described in Ref. [37], for the calculations focusing on higher vibrational states. The truncation eliminates all channels corresponding to Δv and/or $\Delta v' > 1$ transitions. The magnitude of the inelastic cross sections for collisions of $H_2(v, j = 0)$ with $H_2(v', j = 0)$ depends strongly on the initial vibrational states of the colliding molecules which is consistent with the previous analysis of vibrational relaxation in H-H_2 [7], He-H_2 [8], and Li-Li_2 [10] collisions. For $v = [1 - 6]$ and $v' = 0$, the cross sections show a monotonous increase with the vibrational quantum number v as observed for He-H_2 collisions [8] at ultralow energies. When both molecules are initially vibrationally excited as in $v = [2 - 4]$ and $v' = 1$, the inelastic cross sections become significantly larger and less sensitive to the initial vibrational levels of the two molecules. For

collisions of $H_2(v, j = 2)$ with $H_2(v', j = 0)$, the inelastic cross sections are quite large and show a slight increase with the vibrational quantum numbers. Finally, for collisions of $H_2(v, j = 0)$ with $H_2(v', j = 2)$, the inelastic cross sections are very large due to the near-resonant energy transfer and do not display any particular dependence on the vibrational levels. We have found that the elastic cross sections generally do not depend strongly on the vibrational excitation of the molecules. They rather depend on quantum statistics effect, whether or not the vibrational and rotational quantum numbers of the colliding molecules are the same [38]. This difference can be seen in the elastic cross sections of (0000) and (1000) in Fig. 1.

In summary, we have presented the first study of vibrational relaxation in cold and ultracold molecule - molecule collisions and found a new mechanism of state selective ro-vibrational energy transfer. If the colliding molecules are in different levels of vibrational and rotational excitation, the ro-vibrational energy may be efficiently exchanged between the molecules, leading to near-resonant energy transfer. If the molecules are distinguishable, this process corresponds to rotational energy transfer from one vibrational state of the colliding molecules to another. This inelastic process that dominates over all other inelastic transitions is largely insensitive to the initial vibrational excitation of the molecules. The process may be an important mechanism for collisional energy transfer in ultracold molecules formed by photoassociation of ultracold atoms and for chemical reactions producing identical molecules. We hope that these results will stimulate further studies of vibrational energy transfer in molecular collisions at ultracold temperatures.

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